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(54) Photocurable electroconductive
coating compositions

(57) The compositions are formulated with silver powder comprising aggregate or clustered particles, as electroconductivity-imparting agent, in combination with a photocurable vehicle resin and a photosensitizer. Ultraviolet light can penetrate relatively thick layers of the compositions through the interstices of the aggregate silver particles to efficiently cure the deepest parts of the layers. In the prior art, conventional silver-containing coating

compositions do not have satisfactory photocurability due to the reflection or absorption of ultraviolet light by the conductive particles.

The silver powder of aggregate particles is prepared by heating ordinary silver powder in an atmosphere of non-oxidizing or reducing gas or, more conveniently, by the reduction of silver oxide, formed by the reaction of silver nitrate and sodium hydroxide, with formaldehyde in an aqueous medium, the concentration of the individual reactants and the molar ratio of the reactants being controlled within narrow limits.

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SPECIFICATION

Photocurable electroconductive coating compositions

The present invention relates to a method for the preparation of a silver powder of aggregate particles and a photocurable electroconductive coating composition formulated with the silver powder.

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As is well known, most of the prior art electroconductive coating compositions are prepared by dispersing various kinds of electroconductivity-imparting agents, such as powders of metals, e.g. silver, copper and the like, and carbon powders, in a vehicle. The vehicle resins used in the conventional electroconductive coating compositions belong to the class of thermosetting resins curable by heating at an elevated temperature. One of the problems in such an electroconductive coating composition is that the substrate material which is to be coated with the coating composition is limited to those highly resistant to the heating treatment at the temperature for the curing of the coating composition.

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Accordingly, it has long been desired to develop a photocurable electroconductive coating composition which is curable only by irradiation with light, e.g. ultraviolet light, at room temperature without heating at an elevated temperature which may affect substrate materials with poor heat resistance.

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There is, however, a fundamental difficulty in formulating an electroconductive coating composition with a photocurable resin as the vehicle because of the insufficient curing of the coating composition due to the deficiency of the energy of the ultraviolet light. The light cannot penetrate the coating layer due to the strong reflection on the surface of the metal powder or the strong absorption in the carbon powder so that the photocuring of the coating composition is effected only in the very thin surface layer and the coating composition in the depth of the coating layer is left uncured even by a prolonged irradiation with light. As a consequence, it has been impossible to form an electroconductive coating layer above a certain thickness by use of a conventional photocurable electroconductive coating composition.

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Thus, ways were sought to provide a photocurable electroconductive coating composition capable of being photocured by irradiation with ultraviolet light to a considerable coating layer depth the coating composition being formulated with a silver powder.

The invention thus provides a photocurable electroconductive coating composition, and a method for the preparation of silver powder suitable for formulating in the photocurable electroconductive coating composition.

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The photocurable electroconductive coating composition of the present invention comprises a photocurable vehicle resin and a silver powder of aggregate or cluster particles, optionally in combination with a glass powder.

The silver powder of aggregate or cluster particles can be prepared in several ways. For example, such a powder is obtained by the heat treatment of an ordinary silver powder in an atmosphere of non-oxidizing or, in particular, reducing gas. Alternatively, such a silver powder is prepared most advantageously by the reduction of silver oxide formed by the reaction of silver nitrate with sodium hydroxide in an aqueous solution using formaldehyde as the reducing agent where the molar ratio and the concentration of the individual reactants are within narrow ranges. Thus, 100 parts by moles of silver nitrate in an aqueous solution of 30 to 40% concentration and 150 to 200 parts by moles of sodium hydroxide in an aqueous solution of 16 to 20% concentration are first reacted to form an aqueous slurry of silver oxide (Ag_2O), the aqueous slurry is diluted with water to give a concentration of 3.7 to 7% calculated as Ag_2O and the thus diluted aqueous slurry of Ag_2O is admixed with 60 to 100 parts by moles of formaldehyde in an aqueous solution of 21 to 30% concentration to reduce the silver oxide to elementary silver.

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Preferred embodiments of the invention will now be described.

The inventors have conducted extensive investigations with the object of obtaining a photocurable electroconductive coating composition formulated with silver powder and, on the base of their discovery that the transmission of ultraviolet light through a silver-containing coating composition depends largely on the condition of the silver particles or, in particular, on the configuration of the silver particles, arrived at a conclusion that aggregate or clustered particles or granules of silver are suitable for the purpose, such silver particles being obtained by the heat treatment of ordinary silver powder of discrete particles in a non-oxidizing or reducing gas leading to coalescence of the particles at their contact points with a growing chain structure and final aggregate or clustered particles.

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When such aggregate or clustered particles of silver are dispersed in a vehicle of photocurable resin, the resultant photocurable coating composition is unexpectedly sensitive to irradiation with ultraviolet light and cures to the full depth of a coating layer of considerable thickness.

The starting silver powder to be subjected to the heat treatment in a non-oxidizing or reducing atmosphere may be obtained by any conventional methods including physical or mechanical processes such as atomizing, stamping and the like and chemical processes such as solid state reactions, reduction or thermal decomposition of solid silver salts, and liquid state reactions, e.g. chemical or electrolyte reduction of solutions of silver salts.

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The particle configuration of the starting silver powder is not specifically limitative and may be

spherical, dendritic, flaky or cubic. The particle size of the starting silver powder is also not limited but it is usually in the range from 0.1 to 20 μm for spherical particles and from 3 to 100 μm for the diameter along the longer axis and from 0.1 to 1 μm for the thickness for flaky particles.

- 5 The aggregation of the discrete silver particles is performed by heating the silver powder in an atmosphere of a non-oxidizing or, in particular, reducing gas. The temperature and length of time of the heat treatment may be about the same as in the baking or surface deoxidation of the silver powder and usually in the ranges from 70 to 120°C and from 24 to 48 hours. Several examples of such a non-oxidizing or reducing gas for the heat treatment are given in Table 1 below, in which the composition of the mixed gases is given as % by volume. 5

TABLE 1

| Component | CO ₂ | CO | H ₂ | CH ₄ | H ₂ O | N ₂ |
|-----------------------|-----------------|----------|----------------|-----------------|------------------|----------------|
| Weakly reducing gas | 0.05 | 0.05-1.5 | 1.2-2.0 | 0 | 0 | 89-98 |
| Deoxidation gas No. 1 | 0 | 0 | 75 | 0 | 0 | 25 |
| Deoxidation gas No. 2 | 0.05-2.0 | 0.05-1.0 | 50-99.8 | 0-0.4 | 0-3.5 | balance |
| Carburizing gas | 0.5 | 20-40 | 30 | 3-30 | 0.57 | balance |

When the silver powder is subjected to heat treatment in the atmosphere of the above given mixed gas, the particles of silver begin to be mutually bonded at the contact points to form chains which grow finally into botryoidal aggregates or clusters. The aggregate or clustered particle here mentioned is a silver particle formed by regular or irregular bonding of a number of discrete silver particles. When 15 such aggregate particles are dispersed in a vehicle, the interstices between the aggregate particles are broader (although the distances between the individual base particles have been reduced) than in a dispersion of the same amount of discrete particles as is evidenced by microscopic examination of the dispersions. 15

- 20 The unexpected photosensitivity of the photocurable electroconductive coating composition of the invention derives, presumably, from the fact that the interstices between the aggregate silver particles serve as the path for the ultraviolet light whereas the electroconductivity of the silver-formulated coating composition largely depends on the total content of the silver powder per se. 20

- 25 The silver powder of aggregate particles may be used in combination with ordinary metal powder or carbon powder provided that the presence of the particles of the latter powder is not inhibitive to the photocurability of the vehicle resin. For example, an electroconductive coating composition formulated with the silver powder of aggregate particles in combination with 20% by weight or less of a powder of certain metals such as nickel, zinc, manganese, indium and the like is advantageous in reducing migration of silver. 25

- 30 The silver powder of aggregate particles prepared by the above described aggregation heat treatment is sufficiently effective as an electroconductivity-imparting agent in a photocurable coating composition. The problem with such a silver powder is the relatively high cost of production since the silver powder is produced in two steps, i.e. the preparation of an ordinary silver powder and the subsequent heat treatment of the powder in an atmosphere of non-oxidizing or reducing gas. 30

- 35 Accordingly, the inventors further conducted investigations in order to develop an advantageous process for the production of silver powders of aggregate particles at low cost and they arrived at a process of chemical reduction in an aqueous medium. The process is basically similar to the method described in Japanese Patent Publication 40-6971 according to which silver nitrate and sodium hydroxide are first reacted to form silver oxide which is subsequently reduced with formaldehyde into elementary silver. In the process of the invention, however, the concentration of each of the reactants as 40 well as the molar ratio of the reactants are strictly limited within narrow ranges not described in the above mentioned prior art reference. 40

- 45 Thus, the method of the invention for the preparation of a silver powder of aggregate particles comprises reacting silver nitrate and sodium hydroxide by admixing 100 parts by moles of silver nitrate in an aqueous solution of 30 to 40% concentration and 150 to 200 parts by moles of sodium hydroxide in an aqueous solution of 16 to 20% concentration to form an aqueous slurry of silver oxide (Ag₂O), diluting the aqueous slurry of silver oxide by adding water to give a content of silver oxide of 3.7 to 7% and then reducing the silver oxide by admixing 60 to 100 parts by moles of formaldehyde in an aqueous solution of 21 to 30% concentration. 45

The reaction of silver nitrate and sodium hydroxide is carried out with agitation at a temperature between 20 and 50°C or, preferably, between 20 and 30°C. When the concentration of the aqueous solution of silver nitrate is lower than 30%, aggregate particles of silver are rarely formed whereas a higher concentration than 40% results in a too violent reaction so that agitation of the reaction mixture is insufficient leading to difficulties in the control of the temperature and the formation of too coarse particles.

When the amount of sodium hydroxide is smaller than 150 parts by moles per 100 parts by moles of silver nitrate, the yield of silver powder may be decreased while too large amounts (over 200 parts by moles) lead to coarsening of the silver particles. The concentration of the aqueous solution of sodium hydroxide is limited because a concentration lower than 16% cannot give aggregate particles of silver while a concentration higher than 20% is disadvantageous due to too violent reaction so that agitation may be insufficient and large amounts of coarser particles are formed.

The reaction mixture obtained by the reaction of silver nitrate and sodium hydroxide is an aqueous slurry of silver oxide. When this aqueous slurry of silver oxide is admixed as such with the aqueous solution of formaldehyde, the reduction reaction proceeds too violently and forms coarser particles of silver. When an electroconductive coating composition is prepared by formulating a silver powder of such coarser particles, the electroconductivity of the coating composition is sometimes insufficiently high. It is therefore necessary that the aqueous slurry of the silver oxide is diluted by adding water to give a content of silver oxide in the range from 3.7 to 7%. The lower limit of 3.7% is determined by economic considerations since a lower content of silver oxide requires larger reaction vessels.

The reaction with formaldehyde is carried out at a temperature between 20 and 50°C or, preferably, between 20 and 30°C. When the amount of formaldehyde is smaller than 60 parts by moles or the concentration of the aqueous solution of formaldehyde is lower than 21%, the resultant silver particles are too small in diameter and not aggregated whereas too much formaldehyde (over 100 parts by moles per 100 parts by moles of silver nitrate or higher concentrations than 30%) leads to the formation of coarser particles which in turn result in less satisfactory smoothness of the surface of the coating layer obtained with the coating composition prepared therewith.

When the aqueous slurry of silver oxide, which is alkaline due to the excess amount of sodium hydroxide, is admixed with the aqueous solution of formaldehyde, the alkalinity of the reaction mixture is reduced. It is recommended that the pH value after completion of the reaction is maintained in the range from 7 to 9 by suitably selecting the amount of the aqueous solution of formaldehyde within the above given range. After completion of the reaction, the silver powder formed in the reaction mixture is thoroughly washed with water and dried.

The silver powder of aggregate particles thus prepared can be formulated in the coating composition just in the same manner as with the silver powder obtained by the heat treatment of ordinary silver powder. The amount of the silver powder in the coating composition is usually in the range from 50 to 95% by weight based on the total amount of the photocurable vehicle resin and the silver powder. When the amount is smaller than 50% by weight, the electroconductivity of the resultant coating composition is unduly low whereas larger amounts than 95% by weight are undesirable due to the inferior physical properties of the coating layer as well as decreased workability or printability during coating. The silver powder of aggregate particles can be dispersed in the vehicle uniformly by use of a conventional blending machine such as a roller mill, ball mill, attritor and the like.

The vehicle resin used in the inventive electroconductive coating composition may be conventional photocurable resin without particular limitations. A typical example of composition suitable as the vehicle resin is as follows.

| Component | Amount, % by weight |
|-------------------------------|---------------------|
| Oligomer of a polymer | 30—50 |
| Polyfunctional acrylic ester | 10—30 |
| Monofunctional acrylic ester | 10—40 |
| Non-reactive special additive | 1—20 |
| Photosensitizer | 0.5—20 |

The oligomer of a polymer mentioned above is exemplified by urethane acrylate, melamine acrylate, polyester acrylate, polyester urethane, epoxy acrylate, oligoester acrylate and the like.

The polyfunctional acrylic ester mentioned above is exemplified by 1,6-hexanediol diacrylate, neopentylglycol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate and the like and the monofunctional acrylic ester is exemplified by 2-hydroxyethyl acrylate, 2-ethylhexyl acrylate and the like.

The non-reactive special additive above mentioned includes adhesivity improvers used to increase

the adhesion of the electroconductive coating composition to the substrate surface exemplified by methacryloxyethyl phosphate, silane coupling agents such as β -aminopropyl trimethoxysilane, vinyl triethoxysilane and the like and stabilizers such as N-nitrosophenyl hydroxylamine and the like.

The photosensitizers may be selected according to the type of the vehicle resin from conventional photosensitizers such as benzoin ethers, benzophenone, Michler's ketone, thioxanthone and the like. 5

The coating composition of the present invention prepared as described above may be applied on to a substrate e.g. made of plates of phenolic resins, epoxy resins, ceramics and glass by a conventional coating means such as screen printing, brush coating, die coating and the like in the same manner as with ordinary photocurable coating compositions. The coating layer thus obtained may be irradiated with ultraviolet light of a wavelength of 100 to 400 nm for 5 to 60 seconds to give a cured coating film within short time. This curing effect is obtained by the ultraviolet light passing through the interstices between the aggregate particles of the silver powder to the depth of the coating layer and the photosensitizer contained in the vehicle absorbs the energy of the light and is excited electrically to form free radicals which initiate the polymerization of the vehicle resin. 10

The photocuring of the inventive coating composition can be further accelerated when a suitable amount of glass powder is admixed in the composition. the particles of the glass powder have preferably a dimension of 10 to 100 μ m diameter and the glass powder may be glass beads or chopped glass fibers. The amount of the glass powder is suitably in the range from 1 to 15% by weight based on the amount of the silver powder. When the amount of the glass powder is smaller than 1% by weight, no particular advantage is obtained whereas larger amounts than 15% by weight are undesirable because not only no correspondingly enhanced effect is obtained but also the electroconductivity of the resultant coating layer is decreased. The accelerating effect on curing obtained by the admixture of a glass powder is presumably due to the reflection, diffused reflection or refraction of the ultraviolet light coming into the coating layer by the glass particles so that the light can reach the rear of the silver particles. 15 20 25

When the substrate, e.g. a printed circuit board on which the circuit is formed by printing with the coating composition, is made of a transparent material such as a polyester resin, polyimide resin, parabanic acid and the like, further acceleration of photocuring can be achieved by irradiating the coating layer on the substrate with ultraviolet light from both sides, directly from one side and through the substrate from the other side. 30

The photocured coating film of the coating composition has the advantage of stabilized electroconductivity because the single particles of the silver powder are dispersed in the vehicle not discretely but in the form of entangled chains of the particles to form aggregates or clusters. Further, the coating composition of the invention is, being a photocurable coating composition, advantageous (1) by the absence of the drawbacks such as the distortion, deformation, degradation or inaccurate dimensions of the final product caused in the substrate by baking of the coating composition unavoidable when conventional solution-type or baking-type electroconductive coating compositions are used as well as a stable thickness of the coating layer unaltered by curing, (2) by the improved working environment owing to the absence or small amounts, if present, of volatile organic solvents, and (3) by the improved productivity obtained by the saving of heat energy for curing, decreased cost for curing facilities and shortened curing time, say, one third or shorter, in comparison with the conventional baking-type coating compositions. 35 40

Following are Examples of the present invention to further illustrate the invention in more detail but not to limit the scope of the invention in any way. In the Examples, parts are all given by parts by weight. 45

EXAMPLE 1

Into 30 kg of an aqueous solution of silver nitrate of 30% concentration were introduced successively 24 kg of an aqueous solution of sodium hydroxide of 17% concentration and 5 kg of an aqueous solution of formaldehyde of 20% concentration under agitation while the reaction mixture was kept at 30°C. The silver powder thus formed, filtered, washed and dried had an average particle diameter of about 0.1 μ m. 50

The silver powder is then heated at 80 °C for 24 hours in an atmosphere of the weakly reducing gas as shown in Table 1. The resultant silver powder had an average particle diameter of about 10 μ m and aggregate structure as examined microscopically. 55

A photocurable electroconductive coating composition (designated as Coating Composition A) was prepared by uniformly blending in a roller mill 80 parts of the silver powder of aggregate particles, 10 parts of epoxy acrylate, 9 parts of trimethylolpropane triacrylate and 1 part of benzophenone. For comparison, a similar coating composition (designated as Coating Composition a) was prepared with the same formulation as above except that the silver powder of aggregate particles was replaced with the silver powder of discrete particles before heat treatment. 60

EXAMPLE 2

A melt of silver running out of a nozzle was blown off with a water jet of 300 liters/minute and

scattered in an atmosphere of the deoxidating gas No.1 as shown in Table 1, where the silver powder was kept to simultaneously effect dehydration and drying and the heat treatment. The thus obtained powder had an average particle diameter of about 5 to 10 μm and aggregate structure with large interstices as indicated by the microscopic examination.

- 5 A photocurable electroconductive coating composition (designated as Coating Composition B) 5
was prepared by uniformly blending in a roller mill 75 parts of the silver powder of aggregate particles, 14 parts of polyester acrylate, 10 parts of pentaerythritol acrylate, 0.5 part of thioxanthone and 0.5 part of vinyl triethoxysilane. For comparison, a similar coating composition (designated as Coating Composition b) was prepared with the same formulation as above except that the silver powder of
10 aggregate particles was replaced with a silver powder having an average particle diameter of about 1 μm prepared by water jet scattering in an atmosphere of air instead of the deoxidating gas No.1. 10

EXAMPLE 3

- A photocurable electroconductive coating composition (designated as Coating Composition C) was prepared by uniformly blending in a roller mill 70 parts of the silver powder of aggregate particles prepared in Example 1, 10 parts of glass beads, 10 parts of epoxy acrylate, 9 parts of trimethylolpropane triacrylate and 1 part of benzophenone. 15

EXAMPLE 4

- Two kinds of heat curable electroconductive coating compositions were prepared each by uniformly blending 80 parts of the silver powder of aggregate particles prepared in Example 1 or the silver powder in Example 1 before the heat treatment, 20 parts of a phenolic resin and 20 parts of ethyl alcohol (designated as Coating Compositions E and D, respectively). 20

- Each of the Coating Compositions A, B, C, D, E, a and b prepared as described above was applied on to a plate of phenolic resin by die coating to give a coating layer of 30 μm thickness and subjected to curing. the curing of the Coating Compositions A, B, C, a and b was effected by moving the coated
25 substrate plate at a velocity of 2m/minute under two high-pressure mercury lamps of 80 watts/cm power placed 15 cm above the moving substrate plate and the curing of the Coating Compositions D and E was effected by heating the coated substrate plate in an air oven at 150°C for 30 minutes. 25

- The cured coating films were examined for thickness, hardness and electric resistivity to give the results set out in Table 2 below. The thickness of the cured coating films given in the table was obtained
30 by use of a tester for surface roughness and the hardness was determined in accordance with JIS K 5400 6.14 for pencil hardness. 30

TABLE 2

| Coating composition | A | B | C | a | b | D | E |
|--|--------------------|--------------------|--------------------|-----------|-----------|--------------------|--------------------|
| Thickness of cured coating film, μm | 30 | 30 | 30 | 30 | 30 | 20 | 20 |
| Hardness of cured coating film | 3H | 4H | 5H | Not cured | Not cured | 4H | 4H |
| Electric resistivity, ohm-cm | 1×10^{-3} | 4×10^{-3} | 1×10^{-3} | ∞ | ∞ | 5×10^{-4} | 1×10^{-4} |

- As is clear from the results shown in Table 2, the coating composition in accordance with the present invention is readily cured by irradiation with ultraviolet light to give cured coating films having
35 sufficiently high hardness and electroconductivity while the coating compositions prepared with the silver powders of discrete particles are not curable by irradiation with ultraviolet light. The performance of the cured coating films obtained with the coating compositions of the invention was as good as that obtained with conventional heat-curable coating compositions (coating Compositions D and E). 35

EXAMPLE 5 (Preparation 5)

- An aqueous solution of silver nitrate prepared by dissolving 1000 parts of silver nitrate in 1750 parts of water to give a concentration of 36.4% and a 18.2% aqueous solution of sodium hydroxide 40

prepared by dissolving 400 parts of sodium hydroxide in 1800 parts of water were mixed with agitation at 40 to 50°C to give an aqueous slurry of silver oxide (Ag_2O). The aqueous slurry was diluted by adding 7000 parts of water to give a content of 6.5% as Ag_2O and then a 23.3% aqueous solution of formaldehyde prepared by diluting 400 parts of 35% formalin with 200 parts of water was added to the thus diluted aqueous slurry of silver oxide with agitation at 20 to 50°C. The molar ratio of silver nitrate, sodium hydroxide and formaldehyde ($\text{AgNO}_3/\text{NaOH}/\text{HCHO}$) was 100/170/80 and the pH value of the reaction mixture after completion of the reaction was 8.0

The silver powder formed in the reaction mixture which was separated by filtration, thoroughly washed and dried at 80 °C for 24 hours had a particle diameter ranging from 10 to 20 μm and was found to have an aggregate structure as examined with a scanning electron microscope.

EXAMPLE 6 (Preparation 6—1 to 6—4)

The procedure for the preparation of silver powder was substantially the same as in Example 5 above with varied formulations for the reactant solutions. The formulation as well as the particle diameter and the condition of particles of the resultant silver powders are summarized in Table 3.

As is clear from the results shown in Table 3, the silver powders obtained in Preparations 6—1 and 6—2 had a particle diameter suitable for use in the formulation as electroconductive coating compositions and had an aggregate structure formed by irregular coalescence of the single particles of silver while the silver powders obtained in Preparations 6—3 and 6—4, where the concentration of the silver nitrate solution was either too low or too high, had too small or too large particle diameter, respectively, and the particles were also not in aggregate structure.

TABLE 3

| Preparation No. | | 6—1 | 6—2 | 6—3 | 6—4 |
|---|-------------------------------|------------|------------|------------|------------|
| Silver nitrate solution | Silver nitrate taken, parts | 100 | 100 | 100 | 100 |
| | Water taken, parts | 200 | 150 | 250 | 100 |
| | Concentration, % | 33.3 | 40.0 | 28.6 | 50.0 |
| Sodium hydroxide solution | Sodium hydroxide taken, parts | 40 | 40 | 40 | 40 |
| | Water taken, parts | 180 | 180 | 180 | 180 |
| | Concentration, % | 18.2 | 18.2 | 18.2 | 18.2 |
| Water added to the slurry, parts | | 700 | 700 | 700 | 700 |
| Silver oxide in the slurry, % | | 6.3 | 6.6 | 6.0 | 7.0 |
| Formaldehyde solution | 35% formalin taken, parts | 40 | 40 | 40 | 40 |
| | Water taken, parts | 20 | 20 | 20 | 20 |
| | Concentration, % | 23.3 | 23.3 | 23.3 | 23.3 |
| $\text{AgNO}_3/\text{NaOH}/\text{HCHO}$ molar ratio | | 100/170/80 | 100/170/80 | 100/170/80 | 100/170/80 |
| Particle diameter, μm | | 5—20 | 10—30 | 0.1—10 | 100—200 |
| Particle configuration | | Aggregate | Aggregate | Discrete | Discrete |

EXAMPLE 7 (Preparations 7—1 to 7—4)

The procedure for the preparation of silver powder was substantially the same as in Example 5 though with varied formulations for the reactant solutions. The formulation as well as the particle diameter and the condition of particles of the resultant silver powders are summarized in Table 4.

As is clear from the results shown in Table 4, the silver powders obtained in Preparations 7—1 and 7—2 had an adequate particle diameter and an aggregate structure while the silver powders obtained in Preparations 7—3 and 7—4, where the concentration of the sodium hydroxide solution was either too high or too low, had a too large or too small particle diameter, respectively, and the particles were also not in aggregate structure.

EXAMPLE 8 (Preparations 8—1 to 8—6)

The procedure for the preparation of silver powders was substantially the same as in Example 5 though with varied formulations for the reactant solutions. The formulation as well as the particle diameter and the condition of particles of the resultant silver powders are summarized in Table 5 below.

TABLE 4

| Preparation No. | | 7—1 | 7—2 | 7—3 | 7—4 |
|--|-------------------------------|------------|------------|------------|------------|
| Silver nitrate solution | Silver nitrate taken, parts | 100 | 100 | 100 | 100 |
| | Water taken, parts | 175 | 175 | 175 | 175 |
| | Concentration, % | 36.4 | 36.4 | 36.4 | 36.4 |
| Sodium hydroxide solution | Sodium hydroxide taken, parts | 38 | 47 | 40 | 40 |
| | Water taken, parts | 180 | 200 | 120 | 240 |
| | Concentration, % | 17.1 | 19.0 | 25.0 | 14.3 |
| Water added to the slurry, plate | | 700 | 750 | 700 | 700 |
| Silver oxide in the slurry, % | | 6.5 | 6.1 | 6.9 | 6.1 |
| Formaldehyde solution | 35% formalin taken, parts | 40 | 40 | 40 | 40 |
| | Water taken, parts | 20 | 20 | 20 | 20 |
| | Concentration, % | 23.3 | 23.3 | 23.3 | 23.3 |
| AgNO ₃ /NaOH/HCHO molar ratio | | 100/160/80 | 100/200/80 | 100/170/80 | 100/170/80 |
| Particle diameter, μ m | | 10—20 | 10—30 | 100—200 | 0.1—10 |
| Particle configuration | | Aggregate | Aggregate | Discrete | Discrete |

As is clear from the results shown in Table 5, the silver powders obtained in Preparations 8—1 and 8—2 had an adequate particle diameter and an aggregate structure while the silver powders obtained in the other Preparations were not suitable for use in electroconductive coating compositions. For example, the silver powders obtained in Preparations 8—3 and 8—4, where the concentration of the formaldehyde solution was either too high or too low, had a too large or too small particle diameter and

the particles were not in aggregate structure. In Preparation 8—5, where the dilution of the aqueous slurry of silver oxide with water was insufficient, the agitation of the reaction mixture was carried out with difficulty and the resultant silver powder was somewhat blackish imparting the coating composition formulated therewith rather poor electroconductivity. The silver powder obtained in Preparation 8—6, where the amount of formaldehyde was too small, had a too small particle diameter and the particles were not in aggregate form so that the powder was not suitable for use in electroconductive coating compositions.

EXAMPLE 9

- Photocurable electroconductive coating compositions were prepared each by uniformly blending in a roller mill the silver powder prepared in Preparation 5, 8—2, 6—3 or 8—3 and the other ingredients as indicated in Table 6 below.

TABLE 5

| Preparation No. | | 8—1 | 8—2 | 8—3 | 8—4 | 8—5 | 8—6 |
|--|-------------------------------|-----------|-----------|----------|----------|------------|----------|
| Silver nitrate solution | Silver nitrate taken, parts | 100 | 100 | 100 | 100 | 100 | 100 |
| | Water taken, parts | 175 | 175 | 175 | 175 | 175 | 175 |
| | Concentration, % | 36.4 | 36.4 | 36.4 | 36.4 | 36.4 | 36.4 |
| Sodium hydroxide solution | Sodium hydroxide taken, parts | 40 | 40 | 40 | 40 | 40 | 40 |
| | Water taken, parts | 180 | 180 | 180 | 180 | 180 | 180 |
| | Concentration, % | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 |
| Water added to the slurry, parts | | 700 | 700 | 700 | 700 | 560 | 700 |
| Silver oxide in the slurry, % | | 6.5 | 6.5 | 6.5 | 6.5 | 7.5 | 6.5 |
| Formaldehyde solution | 35% formalin taken, parts | 33 | 40 | 40 | 40 | 40 | 28 |
| | Water taken, parts | 20 | 10 | 50 | 30 | 20 | 20 |
| | Concentration, % | 21.7 | 28.0 | 31.1 | 20.0 | 23.3 | 20.4 |
| AgNO ₃ /NaOH/HCHO molar ratio | | 100/170 | 100/170 | 100/170 | 100/170 | 100/170 | 100/170 |
| Particle diameter, μ m | | 165 | 180 | 180 | 180 | 180 | 155 |
| Particle configuration | | 5—20 | 10—30 | 50—100 | 0.1—10 | — | 0.1—10 |
| | | Aggregate | Aggregate | Discrete | Discrete | (See text) | Discrete |

The coating compositions thus prepared were applied on a substrate plate of a phenolic resin by die coating to give a film thickness of 30 μ m and irradiated with ultraviolet light by moving at a velocity of 2m/minute under two high-pressure mercury lamps of 80 watts/cm placed 15 cm above the moving substrate.

The thus photocured films of the electroconductive coating compositions were examined for thickness, pencil hardness and electric resistivity in the same manner as in Example 4 to give the results shown in Table 6.

TABLE 6

| | | | | | | |
|------------------------------------|------------------------------|--------------------|--------------------|--------------------|-----------|--------------------|
| Silver powder, parts | Preparation No. 5 | 80 | — | 70 | — | — |
| | Preparation No. 8-2 | — | 77 | — | — | — |
| | Preparation No. 6-3 | — | — | — | 80 | — |
| | Preparation No. 8-3 | — | — | — | — | 77 |
| Epoxy acrylate, parts | | 10 | — | 10 | 10 | — |
| Urethane acrylate, parts | | — | 11 | — | — | 11 |
| Trimethylolpropane acrylate, parts | | 9 | — | 9 | 9 | — |
| 2-Hydroxyethyl acrylate, parts | | — | 11 | — | — | 11 |
| Benzophenone, parts | | 1 | — | 1 | 1 | — |
| Michler's ketone, parts | | — | 1 | — | — | 1 |
| Glass beads, parts | | — | — | 10 | — | — |
| Cured coating film | Pencil hardness | 3H | 3H | 5H | Not cured | Insufficient cure |
| | Electric resistivity, ohm-cm | 1×10^{-3} | 3×10^{-3} | 1×10^{-3} | ∞ | 1×10^{-3} |

CLAIMS

- 5 1. A photocurable electroconductive coating composition which comprises: 5
 - (a) a silver powder of aggregate particles,
 - (b) a photocurable vehicle resin, and
 - (c) a photosensitizer.
2. A electroconductive coating composition which comprises:
 - 10 (a) a silver powder of aggregate particles. 10
 - (b) a photocurable vehicle resin,
 - (c) a photosensitizer, and
 - (d) a glass powder.
3. The photocurable electroconductive coating composition as claimed in claim 1 or claim 2
 - 15 wherein the amount of the silver powder of aggregate particles is in the range from 50 to 95% by weight based on the total amount of the photocurable vehicle resin and the silver powder. 15
4. The photocurable electroconductive coating composition as claimed in claim 2 wherein the glass powder has a particle diameter in the range from 10 to 100 μm .
5. The photocurable electroconductive coating composition as claimed in claim 2 wherein the
 - 20 amount of the glass powder is in the range from 1 to 15% by weight based on the amount of the silver powder of aggregate particles. 20
6. A method for the preparation of a silver powder of aggregate particles which comprises:
 - (a) reacting silver nitrate and sodium hydroxide by admixing 100 parts by moles of silver nitrate as an aqueous solution of a concentration in the range from 30 to 40% by weight and from 150 to 200 parts
 - 25 by moles of sodium hydroxide as an aqueous solution of a concentration in the range from 16 to 20% by weight to form an aqueous slurry of silver oxide, 25
 - (b) diluting the aqueous slurry of silver oxide by adding water to give a content of the silver oxide in the range from 3.7 to 7% by weight, and
 - (c) reacting the silver oxide in the thus diluted aqueous slurry with formaldehyde by adding from 60 to
 - 30 100 parts by moles of formaldehyde as an aqueous solution of a concentration in the range from 21 to 30% by weight into the aqueous slurry to form elementary silver. 30

7. The method as claimed in claim 7 wherein the reaction of silver nitrate and sodium hydroxide is carried out at a temperature in the range from 20 to 30°C.

8. A method as claimed in 7 wherein the reaction of silver oxide and formaldehyde is carried out at a temperature in the range from 20 to 30°C.

5 9. The method as claimed in claim 7 wherein the amount of formaldehyde is such that the reaction mixture after completion of the reaction of silver oxide and formaldehyde has a pH value in the range from 7 to 9. 5

10 10. A method for the preparation of a silver powder of aggregate particles which comprises heating a silver powder of discrete particles in an atmosphere of a reducing gas at a temperature in the range from 70 to 120 °C and from 24 to 48 hours. 10

11. A silver powder of aggregate particles when prepared by a method as claimed in any one of Claims 6—10.

12. The photocurable electroconductive coating composition as claimed in any one of Claims 1—5 wherein the silver powder is as claimed in Claim 11.

15 13. The photocurable electroconductive coating composition as claimed in Claim 1 substantially as described in any of the Examples. 15

14. The method as claimed in Claim 5 substantially as described in any of the Examples.

15. A substrate which has been coated with a composition as claimed in any one of Claims 1—5 and 13.